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(54) **Process for preparing an electrochemical catalyst.**

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It is an object of the present invention to provide a process for preparing a catalyst comprising a metal, in particular, a noble metal that is very finely dispersed on a support, with the catalyst being capable of promoting the electrochemical oxidation of hydrogen as well as the electrochemical reduction of oxygen.

Catalysts consisting of noble metals such as platinum deposited on an inert support are typically in the form of a dispersion with a low metal content (around 1% by weight) on a solid with a high specific surface area (i.e. 500 to 1,500 m<sup>2</sup>/g). In most cases such supports have a microporous texture. This creates problems associated with the diffusion of reagents and reaction products via mass transfer into microcapillaries during the use of such catalysts. Understandably, therefore, it is desirable to prepare catalysts on supports of very low porosity or even zero porosity in order to avoid such problems. Such supports typically have a low surface area, on which it is much more difficult to disperse the noble metal in an efficient and hence more economical manner.

Furthermore, to be able to produce a sufficient active mass in applications where a relatively thin catalyst bed has to be utilized, it is important to use a high concentration of metal, and this concentration may be considerably higher than 10% on the support; the latter consideration is particularly relevant in case of thin electrodes of fuel cells.

In fact, in order to obtain maximum catalytic activity in conjunction with the smallest ohmic drop possible and limited installation space requirements, it is necessary to concentrate a sufficient amount of the electrocatalytically active compound (about 0.1 to 1 mg/cm<sup>2</sup>) within the narrow thickness (50 to 200 microns) of the porous electrode.

When traditional methods of supported catalyst preparation are used, these two conditions, i.e., on the one hand, using a support of low or zero microporosity and consequently of moderate specific surface area that is generally less than about 500 m<sup>2</sup>/g, and, on the other hand, providing a high content of the active element, lead to a state of division that is too coarse, resulting in a very inadequate use of noble metals.

The method contemplated by the Applicant permits preparation of well-dispersed catalysts with a high content of noble metal both on supports with a large surface area, in particular, on the order of 1000 m<sup>2</sup>/g, and on supports of a lesser specific surface area, 75 to 500 m<sup>2</sup>/g, to be precise.

Thus, it is an object of the invention to provide a process for preparing an electrochemical catalyst, wherein the following consecutive steps are carried out:

- placing a support in a vessel maintained under a reduced pressure of 10<sup>-1</sup> to 10<sup>-6</sup> torr and a temperature of 100 to 1000°C, which are maintained for 2 to 100 hours,
- allowing the support to cool to ambient temperature under the reduced pressure,
- bringing the vessel to atmospheric pressure by introducing an inert gas free of any condensable impurities,
- impregnating the support with a solution of a metal salt under vigorous agitation so as to obtain a viscous paste,
- freezing the paste by immersion into liquid nitrogen,
- drying the thus frozen paste by freeze-drying until a fine powder is obtained,
- immediately reducing the fine powder under a hydrogen atmosphere at a reduction temperature of 150 to 600°C maintained for 10 minutes to 5 hours,
- allowing the reduced powder to cool to ambient temperature, preferably under a neutral atmosphere, and

passivating the reduced powder and cooling, preferably under an inert atmosphere, by the controlled introduction of oxygen.

The support is made up of finely divided carbon with a specific surface area of at least  $75 \text{ m}^2/\text{g}$ .

Furthermore, the metal salt is a salt of a metal selected from the group comprising platinum, ruthenium, palladium, rhodium, and iridium.

The following examples are provided to give a better idea of the present invention and its advantages with the understanding that these examples are merely illustrative and are in no way limiting in nature.

According to the invention, first of all, all impurities that might have accumulated in the process of prior manipulations are removed from the surface of the catalyst support. The support is, for instance, a carbon black with a specific surface area of at least  $75 \text{ m}^2/\text{g}$ .

To that end, the support is placed in a vessel under reduced pressure on the order of  $10^{-1}$  to  $10^{-6}$  torr, at a temperature of 100 to  $1000^\circ\text{C}$ , or more preferably, 150 to  $600^\circ\text{C}$ , with such conditions maintained until the support reaches a constant weight. This operation typically lasts between 2 and 100 hours and most often for about 15 hours.

Subsequently, cooling is carried out under reduced pressure before bringing the vessel back to atmospheric pressure by introducing an inert gas (e.g. nitrogen) free of any condensable vapors.

Immediately after this operation, a preferably aqueous solution of a noble metal salt, e.g. chloroplatinic acid or platinum chloride, is used to impregnate the support under vigorous agitation, with the volume of the solution being such that a viscous paste is obtained at the end of the operation.

In addition to the above-mentioned salts, it is possible to use a nitrate and, in general, any salt soluble in an aqueous medium or in any other arbitrary solvent, such as, in particular, methanol or acetone.

The viscous paste is then instantly frozen by immersion into liquid nitrogen and dried by freeze-drying.

The fine powder resulting from the latter operation is immediately reduced under a hydrogen atmosphere at a temperature of about  $300^\circ\text{C}$  maintained for 2.5 hours, with such operating conditions being variable between 150 and  $600^\circ\text{C}$  in terms of temperature and between 10 minutes and 5 hours in terms of time.

It should be noted, however, that the rate of temperature rise during the reduction is high, on the order of  $10^\circ\text{C}/\text{min}$ , and may vary between 2 and  $20^\circ\text{C}/\text{min}$ . Likewise, a high hourly flow rate of hydrogen is used, ranging from 2 and 20 times the stoichiometric quantity.

Finally, a controlled introduction of air or oxygen into the reduction vessel is carried out after cooling the latter, preferably under an inert atmosphere, in order to passivate the powder by the controlled oxidation of metal particles.

The catalyst thus obtained is made up of a fine dispersion of platinum crystallites on the carbon. The developed metal surface, as measured by hydrogen chemisorption, is between 60 and  $220 \text{ m}^2/\text{g}$  (for catalysts containing 20% platinum) depending on the nature of the support and depending on the treatment the latter may have been subjected to previously. The developed surfaces effectively correspond to the mean diameters of platinum crystallites of 40 and  $10 \text{ \AA}$ , respectively. These values have been confirmed by

electron microscopy measurements. In particular, it has been observed that in case of the best-dispersed catalysts, the size of the platinum particles does not exceed 12 Å.

The degree of dispersion of such catalysts is therefore very high even when the support has a maximum specific surface area of 100 m<sup>2</sup>/g or less.

In addition, their noble metal concentration is very high. It is typically 20% by weight, but in certain cases it may reach 50%.

In the above, it was presumed that the noble metal used was platinum.

It will be understood that other metals can be used under similar conditions without departing from the spirit of the invention.

Examples include, in particular, ruthenium, palladium, rhodium and iridium.

To further clarify the above, some typical characteristics and properties of catalysts prepared by the Applicant in accordance with the process of the invention are summarized in the tables below.

TABLE I

SUPPORT	S (m <sup>2</sup> /g)	PLATINUM COMPOUND	A (m <sup>2</sup> /g)
Carbolac I	950	H <sub>2</sub> PtCl <sub>6</sub>	195
Carbolac I	950	PtCl <sub>4</sub>	215
Vulcan XC 72	230	H <sub>2</sub> PtCl <sub>6</sub>	80
Vulcan XC 72	230	PtCl <sub>4</sub>	60

In particular, the following parameters are reported in Table I depending on the nature of the support used and the utilized platinum compound:

S: the specific surface area of the support measured by the B.E.T. method using the nitrogen adsorption isotherm at -195°C.

A: the metallic surface area of the metal (m<sup>2</sup> per gram of metal), measured by hydrogen chemisorption at ambient temperature.

In such catalysts, the weight ratio of the weight of platinum to the weight of the catalyst is 20%.

The carbon blacks used as supports are supplied by the Cabot Corporation.

Table II

T%	A (m <sup>2</sup> /g)
2	260
5	265
10	220
20	190
30	155
40	165
50	120

Parameter A, as defined above, is reported in Table II for different values of the weight ratio T% of the weight of platinum to the weight of the catalyst. In this case, the support is Carbolac I with a specific surface area of 950 m<sup>2</sup>/g.

Table III

T%	A (m <sup>2</sup> /g)
2	100
10	90
20	80
40	55

The same parameter is reported in the table above. In this case, the support is Vulcan XC72 with a specific surface area of 230 m<sup>2</sup>/g.

TABLE IV

Support	Supplier	S (m <sup>2</sup> /g)	A (m <sup>2</sup> /g)
Neo Spectra I	Columbian C	1065	170
Carbolac I	Cabot	950	190
Super Spectra	Columbian C	740	170
Regent Super	Degussa	710	160
Neo Spectra III	Columbian C	535	175
Graphite HS	Non-commercial	500	140
Super carbovar	Cabot	400	150
Neo Spectra IV	Columbian C	335	145
Vulcan XC72	Cabot	230	80
Vulcan P	Cabot	150	70
SAFN 110	Ashland	150	85
Vulcan 6F	Cabot	115	70
Mogul L	Cabot	115	75
Elftex S	Cabot	75	65

The values of parameters S and A are reported in Table IV for various types of commercially available supports and T=20%.

The catalysts of the present invention exhibit excellent performance in electrochemical reactions.

They can be used in applications such as, but not limited to, the electrochemical oxidation of hydrogen and the electrochemical reduction of oxygen in fuel cells, in particular.

It will be understood that the invention is not limited to the embodiments and examples described above and covers all modifications thereof.

## CLAIMS

1. A process for preparing an electrochemical catalyst, wherein the following consecutive steps are carried out:
  - placing a support in a vessel maintained under a reduced pressure of  $10^{-1}$  to  $10^{-6}$  torr and a temperature of 100 to 1000°C, which are maintained for 2 to 100 hours,
  - allowing the support to cool to ambient temperature under the reduced pressure,
  - bringing the vessel to atmospheric pressure by introducing an inert gas free of any condensable impurities,
  - impregnating the support with a solution of a metal salt under vigorous agitation so as to obtain a viscous paste,
  - freezing the paste by immersion into liquid nitrogen,
  - drying the thus frozen paste by freeze-drying until a fine powder is obtained,
  - immediately reducing the fine powder under a hydrogen atmosphere at a reduction temperature of 150 to 600°C maintained for 10 minutes to 5 hours,
  - allowing the reduced powder to cool to ambient temperature, preferably under a neutral atmosphere, and
  - passivating the reduced powder and cooling, preferably under an inert atmosphere, by the controlled introduction of oxygen.
2. The process according to claim 1, wherein the reduction temperature is reached by starting from the ambient temperature at a rate of 2 to 20°C/min, with the hydrogen atmosphere maintained using an hourly flow rate of hydrogen of 2 to 20 times the stoichiometric quantity.
3. The process according to any one of claims 1 or 2, wherein the metal salt is a salt of a metal selected from the group comprising platinum, ruthenium, palladium, rhodium, and iridium.
4. The process according to claim 3, wherein the metal is platinum.
5. The process according to any one of claims 1 through 4, wherein the metal salt is selected from the group comprising halides, and, preferably, the chloride, nitrate and other compounds of these metals soluble in a solvent, in particular, in water, methyl alcohol, and acetone.
6. The process according to any one of claims 1 through 5, wherein the ratio between the weight of the metal and the total weight of the catalyst is between 0.01 and 0.5 and is preferably reasonably close to 0.2.
7. The process according to any one of claims 1 through 6, wherein the support is finely divided carbon.
8. The process according to claim 7, wherein the support has a specific surface area of at least 75 m<sup>2</sup>/g.
9. A catalyst obtained by using the process according to any one of claims 1 through 8.
10. A fuel cell utilizing a catalyst according to claim 9.
11. An electrochemical oxidation plant utilizing a catalyst according to claim 9.

12. An electrochemical reduction plant utilizing a catalyst according to claim 9.